IONIZATION IN REACTING GASES

By A. Keith Brewer*

Abstract

Ionization associated with the oxidation of ethyl alcohol in contact with electrodes.—Previous work had shown that various gaseous reactions are accompanied by ionization. The oxidation of ethyl alcohol was chosen because of its simplicity. Nitrogen carrying 3 cc of alcohol per minute and also dry oxygen at the rate of 200 cc per minute were sent into a reaction chamber between two concentric cylindrical electrodes. The currents were measured with an electrometer provided with a radioactive shunt. Although potential differences up to 1800 volts (2400 volts per cm) were used, the current was always proportional to the voltage, being evidently far from saturation. The variation with temperature, 150° to 330°C, was exponential, increasing in the case of gold electrodes 20 fold from 200° to 320°C. With Al electrodes the current was only 1/25th as great, and chemical analysis of the products of reaction indicated that the oxidation was also greatly reduced. The results show that the reaction occurs at the electrode surfaces, the rate depending on the material and on the temperature, and that both positive and negative ions are produced. The absence of saturation is probably due to the ions being formed so close to the surface. Copper electrodes gave anomalous results, a negative Cu electrode behaving like Au while a positive Cu electrode behaved like Al. A soft glass electrode behaved like gold, except that the logarithmic increase with temperature was twice as fast for the negative as for the positive electrode.

ALTHOUGH the production of gaseous ionization by means of chemical action has received the attention of a large number of investigators since the time of Lavoisier, the problem is as yet but little understood. Richardson has pointed out the close relationship existing between this chemical effect and the photo-electric and thermionic effects, although the effects in themselves are separate and distinct.[1]

In previous papers[2,3] it has been shown that both endothermic and exothermic gaseous reactions are accompanied by ionization; that the number of ions formed is proportional to the number of molecules reacting, and that the ionic current observed is proportional to the applied voltage over the range investigated.

It is the purpose of the present paper to present evidence which will throw further light upon the production of gaseous ions by purely

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[1] See "Emission of Electricity from Hot Bodies," by O. W. Richardson for a brief discussion of the history of the subject.

[2] A. K. Brewer and Farrington Daniels, Trans. Amer. Electrochem. Soc. **44**, 257 (1923).

[3] A. Keith Brewer, J. Am. Chem. Soc. **46**, 1403 (1924).

chemical means. Confusing complications have been reduced to a minimum by confining the study to the oxidation of ethyl alcohol vapor at temperatures well below that of ignition. There appeared to be no accompanying phenomena which could give rise to the ionization observed.

Apparatus

The apparatus used in the present research was similar to that described elsewhere.[2] Several minor improvements were added which made it possible to study the ionization in reactions even at dull red heat, and which increased the sensitivity so that currents as small as 10^{-15} amp. could be read with a reasonable degree of accuracy. The electrometer was of a modified Compton design capable of a sensitivity of over 60,000 mm per volt. The resistance of the radioactive leak, shunted across the electrometer circuit, was 2.66×10^{11} ohms. The gold electrodes were the same as those used in the previous research. Potential was supplied to the electrodes by a bank of Burgess B batteries. A copper-constantan thermocouple, enclosed in a thin walled Pyrex tube, was placed in the reaction chamber in such a manner that the temperature of either the outer, or the inner electrode, or of the reacting gas could be measured.

The Reaction

The ionization was produced by the oxidation of absolute ethyl alcohol at various temperatures below that of ignition. A stream of dry oxygen was admitted to the reaction chamber through one of the inlet tubes, while a stream of nitrogen saturated with alcohol vapor was admitted through the other. The reaction, therefore, took place between the electrodes, and in contact with only the electrodes. The oxygen supply was maintained constant at 200 cc per minute, which was far in excess of that necessary for complete oxidation of the alcohol. The rate of flow of the alcohol vapor was calculated from its vapor pressure to be 3 cc per minute.

Experimental Procedure

The ionization which resulted from the oxidation of the alcohol was observed for various electrode potentials, various temperatures of the reacting mixture, and various potential drops between the electrodes. Only one factor was varied at a time in a single set of experiments.

The procedure employed was to adjust the spot of light from the electrometer to a suitable position on the scale by means of the radioactive leak. A supply of oxygen was then admitted to the reaction

chamber through one of the inlet tubes while nitrogen was admitted through the other. No deflection of the electrometer took place. A stop cock was then turned so as to cause the nitrogen to flow through a column of alcohol before entering the reaction chamber. Any ionization that might result from bubbling was removed by passing the vapor through a long tube filled with glass wool, and heated to 200°C. Blank experiments at low temperatures showed the alcohol vapor to be free from any initial ionization. A small induction kick was always noted upon changing the gas entering the reaction chamber; this was readily distinguished from an ionization current.

Upon admitting the alcohol vapor to the reaction chamber a definite deflection of the electrometer was observed, which remained fixed as long as the temperature or the supply of reacting gases was unchanged. When the supply of alcohol was shut off the electrometer returned to the original position. If the supply of oxygen was removed while the flow of alcohol and nitrogen was kept constant, the electrometer never returned quite to the original zero. This was probably due to the fact that the reaction chamber was open at one end so small amounts of oxygen were always present.

The value of the current flowing between the electrodes was calculated by Ohm's law from the known resistance of the radioactive shunt and the voltage as given by the electrometer.

The electrometer was used under both positive and negative control, varying in sensitivity from 6,000 to 36,000 mm per volt. It was found most satisfactory to use positive control and a sensitivity of about 10,000. Since a short electrometer scale was used, the currents observed gave more than full scale deflection for all except the lower applied voltages. For larger currents the electrometer was used as a zero instrument by adjusting the radioactive leak.

The Effect of Temperature

The effect of temperature on the conductance of the reacting mixture of alcohol and oxygen, between gold electrodes, is shown in Fig. 1. The temperature given is that of the outer electrode, which is higher than that of the gas and the inner electrode. The voltage applied to the outside electrode and the supply of gas were kept constant; the temperature alone was varied. Ionization became detectable at about 150°C, and thereafter increased nearly exponentially with the temperature. For a 10° rise in temperature the conductance increased about 22 percent. The sign of the charge applied to the outer electrode changed only the

direction of the ionic current and did not effect its magnitude or the temperature at which it became detectable.

The Effect of Voltage

In Fig. 2 are given the results obtained with gold electrodes, when the supply of reacting gases is maintained constant and the mean potential gradient through the reaction chamber is varied from 0 to $\pm 2{,}400$ volts per centimeter. The observed current is directly proportional to the applied voltage, within the limits of experimental error. Although not shown on the curve, the readings were extended down to 2 volts per

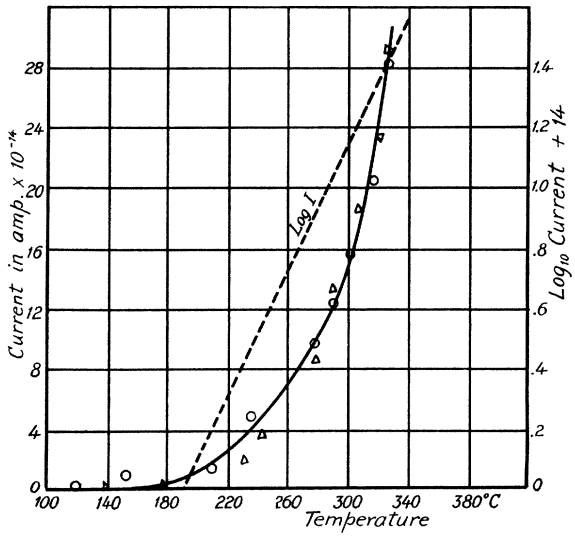

Fig. 1. Potential drop between electrodes 225 volts.
○ Outer electrode negative. △ Outer electrode positive.

centimeter potential gradient and the straight line relation was found still to hold. In these experiments the temperature of the reaction chamber was maintained as nearly constant as possible. The temperature of the gas and of the inner electrode was 200°C; that of the outer electrode was 260°C. A slight rise in temperature was always noted during the course of the reaction.

A chemical analysis of the products of the oxidation could not be made satisfactorily. However qualitative tests showed that a small amount of the alcohol was oxidized to aldehyde, to acid, and to carbon dioxide. A quantitative determination was made of the acid.

Since both positive and negative carriers are evidently formed in the reaction in practically equal amounts, it follows at once that the phe-

nomenon is ionic and not electronic. At some point during the course of the reaction the molecules involved must be broken up into positive and negative ions. In this respect the present reaction appears to differ from the reaction studied by Richardson,[4] and by Brotherton.[5] Information regarding the chemical nature of the ions and the conditions necessary for their formation was obtained by changing the material out of which the electrodes were made.

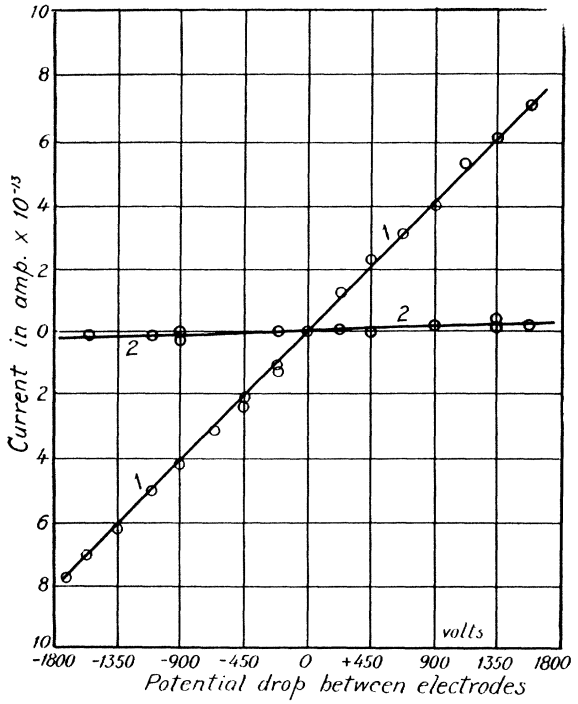

Fig. 2. 1. Gold electrodes; 2. Aluminum electrodes.

The Effect of Changing Electrode Material

Electrodes were constructed of aluminum, of copper, and of soft glass, having the same dimensions as the gold chamber. The glass outer electrode was gold sputtered on the outside to insure better electrical contact with the glass, but the reacting gases, being within the electrode, did not come in contact with the gold film. No difficulty was experienced in using the glass as an electrode for low voltages, because at the temperatures where ionization was detectable the glass was a far better conductor

[4] O. W. Richardson, Phil. Trans. **A222,** 1 (1921).

[5] M. Brotherton, Roy. Soc. Proc. **105,** 468-80 (1924).

than the reacting gas. It was impossible to use the glass at voltages higher than 900 because of electrical leakage from the supports and inlet tubes.

The experiments with the various electrodes were carried out precisely as in the case of the gold chamber. The copper electrodes had to be removed and polished at frequent intervals, because of the formation of a thick film of copper oxide on the surface.

Aluminum electrodes. The results obtained with the aluminum electrodes are shown in Fig. 2. It will be noted that for both positive and negative voltages applied the ionic current was very small, varying from 1 to 5×10^{-15} amp. Little if any rise in temperature was noted when the alcohol was admitted to the reaction chamber.

A chemical analysis of the vapors coming from the aluminum chamber showed the absence of a detectable amount of either aldehyde or acid. The aluminum oxide, therefore, does not behave as a catalyst for the oxidation of alcohol vapor.

From these results it follows that in the case of the gold electrodes the ionization observed during the reaction was not produced in the gas filled space between the electrodes but in immediate contact with the gold surface. With the aluminum electrodes the alcohol-oxygen mixture does not come in actual contact with pure metal but instead with a film of aluminum oxide covering the electrode surface. Since this insulating film of oxide is very thin the capacity between the metal on one side and the gas on the other would of necessity be very high, of the order of a farad. Therefore, if the ions were formed in the gas space between the electrodes, irrespective of the material of the electrodes, the electrometer would indicate their presence as well with the aluminum as with the gold. It would appear from this that, for the catalysis of the reaction and the production of ionization, the alcohol and oxygen must be in actual contact with a conducting surface.

The correctness of the above contention was tested by allowing ozone, which is known to decompose in the gas space, to decompose between the aluminum electrodes. An ionic current was observed almost as large as when ozone decomposed between gold electrodes.

Gold-aluminum electrodes. Since it has been found that ions are not produced from alcohol oxidation in contact with an aluminum electrode, it becomes possible, by the use of one gold and one aluminum electrode, to tell if positive and negative ions are formed in equal quantities at each electrode, and, in the case of the gold, at which electrode the ions are formed to the greater extent.

The results shown in Fig. 3 (curve 1) were obtained when the outer electrode was gold and the inner electrode aluminum. By comparison with Fig. 2 it will be seen that there is no appreciable difference in the resulting ionization, whether the inner electrode is gold or aluminum.

When the outer electrode was aluminum and the inner electrode gold only a very slight current was observed at the temperature used heretofore. When the temperature of the reaction chamber was raised so that the gold inner electrode came to the temperature of the gold outer electrode in the previous experiment, a current was again obtained about equal to that obtained when the electrodes were used in the reverse order.

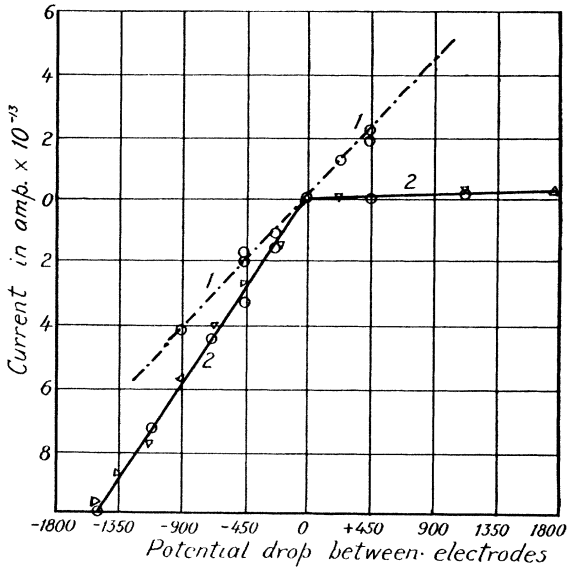

Fig. 3. 1. Gold outside—aluminum inside. 2. O Copper outside and inside; Δ Copper outside—gold outside.

From these data the conclusion follows that both positive and negative ions are formed simultaneously on the same metal surface; also that the ions observed in the experiments with the gold electrodes, were formed largely on the outer electrode. The last result was to be expected, since these experiments were conducted at a temperature but slightly above that at which ionization became observable, and since at this particular temperature, there was a temperature difference between the inner and outer electrode of 60°. The fact that similar results were obtained when the inner electrode was raised to the same temperature as the gold outer electrode in the previous experiments is also interesting. Since the radius of the outer electrode is four times that of the inner, the surface exposed to the reacting gas is four times as great. But, since the

electrodes are concentric cylinders, the fall of potential around the inner electrode is four times that around the outer. The similar results, therefore, indicate that the observable ionization is proportional both to the area of the electrode and to the potential gradient at the electrode.

Copper electrodes. In Fig. 3 (curve 2) are given the results obtained with copper electrodes. It will be seen that when the outer electrode is charged negatively, the conductance through the reacting gas is but slightly larger than that obtained with the gold electrodes, but when a positive charge was placed on the outer electrode, almost no current was observed. The curve is constructed from data obtained with freshly polished surfaces. When the surface was allowed to coat over with a thick film of oxide the observed current often fell off to a quarter of the above value.

The substitution of gold or aluminum for the inner copper electrode had no appreciable effect on the currents observed. The use of an aluminum outer and a copper inner electrode gave the expected results at elevated temperatures; a current was observed when the aluminum was charged positively but none for the opposite sign.

A chemical analysis of the gases passing through the chamber showed that the quantity of alcohol oxidized fell off rapidly as the copper became coated over with oxide. Satisfactory checks were obtained only with the well coated surface, because the experiment had to be run for about ten minutes to get enough of the reacting products for a chemical test. Under these conditions only about a quarter as many molecules of alcohol were oxidized as in the case of the gold surface. The presence of a field of either sign on the outer electrode made no apparent difference in the number of molecules reacting.

The failure to detect ionization when a positive charge was placed on the outer copper electrode is not understood. It is reasonable to suppose that, since ions were present in all of the previous cases when the alcohol was being oxidized, they were also present in this case but did not become freed from the surface layer in which they were formed.

Glass-gold electrodes. In Fig. 4 is shown the current-temperature curve, taken under a potential drop of 300 volts per centimeter, when the outer electrode was glass and the inner electrode was gold. When a positive charge was placed on the glass the ionization curve was almost identical to that obtained with the gold as shown in Fig. 1 except that it began at a slightly higher temperature. For a negative charge on the glass the curve begins at a lower temperature and the logarithmic curve is almost twice as steep.

An accurate current-voltage curve could not be obtained with the glass electrode because of the unsteadiness of the electrometer at high

voltages. From the approximate data, however, it was evident that the straight line relation held as in the previous cases.

The significance of this experiment lies in showing that it is a conducting, and not necessarily a metal, surface that makes possible the escape of ions from the layer of reacting gas.

Discussion of Results

The absence of a saturation current, even at the relatively high voltages used in this research, has a possible explanation in the fact

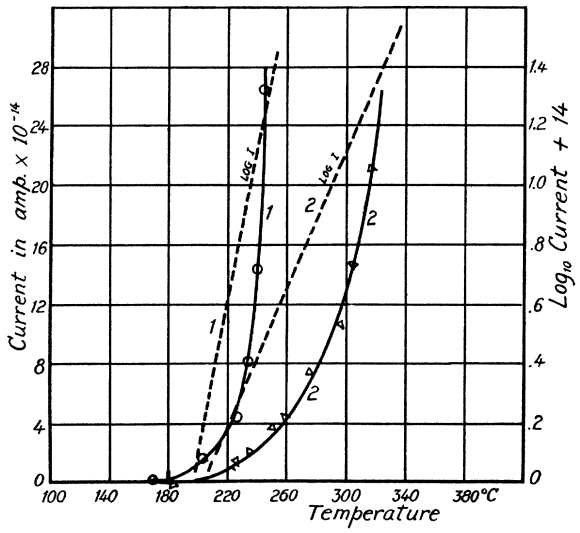

Fig. 4. Potential drop between electrodes 225 volts. 1. Glass electrode negative; 2. Glass electrode positive.

that the source of the ions is in the layer of reacting gases in immediate contact with the electrode surface.

The current observed is constituted by those ions which the field is able to draw away from the reacting layer. However, for the field to draw an ion away from a conductor, it must do so against the electrostatic image of the ion in the conductor. This image force becomes appreciable at a distance of about 10^{-4} cm from the surface. Within this distance the force increases rapidly, i.e., with the inverse square of the distance. Unfortunately, the attractive force cannot be calculated for ions within several molecular diameters of the surface due to the fact that the image forces are overlapped by the stronger molecular forces in the immediate neighborhood of the surface. However, it is reasonable to suppose that an ion at the surface would be held to the surface by a force of several million volts per centimeter.

From the above considerations it becomes apparent that any voltage capable of being used could reach but a short distance into the region in which the image force is appreciable. In fact, only those ions which had moved out to a distance of about 10^{-5} cm from the surface were detected by the highest voltages used in the present research.

If there is a rapid increase in the concentration of ions towards the surface, it would give rise to a straight line relation between current and voltage, with no appearance of saturation. A voltage sufficient to give saturation would be far above that sufficient to cause a spark. Mr. Charles F. Richter has calculated that the concentration of the ions in the layer investigated, increases approximately with the inverse cube of the distance from the surface.

It now becomes possible to suggest an hypothesis for the mechanism of ion formation. A molecule, when driven to the surface of a conductor by kinetic agitation, will be operated on both by the image force of its poles in the conductor, and by the stronger molecular force existing at the surface. (These forces will be entirely independent of any charge placed upon the conductor.) These combined forces will be comparable to the forces holding molecules together. Since the forces acting upon the molecule are electrostatic, the natural consequence is for the molecule to be broken into ions. The ions so formed are then ejected from the surface by kinetic agitation. Ordinarily, the ions, upon being driven from the surface, will recombine to reform the original molecule. Some of the ions, with larger energy content, will be shot out into the fields of other ions, with which they will combine, thus producing chemical reaction. This would explain why only a very small number of the molecules that bombard the surface react chemically.

Mr. Richter has found that if a certain critical velocity of the ions from the surface is necessary for their detection, the variation of the current with the temperature agrees qualitatively with that to be expected from Maxwell's distribution law.

Special acknowledgment is made to Dr. C. F. Burgess, of the Burgess Battery Company, Madison, Wisconsin, for the gift of fifty 45-volt radio B batteries; also to the Department of Physical Chemistry, University of Wisconsin, for the loan of the gold electrodes.

The writer is pleased to take this opportunity to thank Professor R. A. Millikan for his interest in the problem and for his many valuable suggestions.

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June 15, 1925.